Microstructural, Mechanical, and Tribological Properties of Rice Husk Based Carbon: Effect of Carbonizing Temperature

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Microstructural, Mechanical, and Tribological Properties of Rice Husk-Based Carbon: Effect of Carbonizing Temperature

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ABSTRACT

In this study, we investigated the microstructural, mechanical, and tribological properties of rice husk (RH)-based carbon carbonized at various carbonizing temperatures under dry conditions. All samples exhibited amorphous carbon structures and the X-ray diffraction spectra of the samples carbonized at 1300°C and 1400°C indicated the presence of a polymorphic crystal of silica. The hardness increased with temperature due to the densification of the structure and the presence of the hard crystalline silica. At low normal loads, the mean friction coefficient of the material decreased as the carbonizing temperature was increased from 600°C to 800°C and slightly decreased as the carbonizing temperature was further increased from 800°C to 1400°C. At the highest load, all samples, except for that carbonized at 600°C, exhibited low friction coefficients (around 0.10). The wear rates of the all samples were smaller than 10^{-5} $mm^3/N \cdot m$), indicating that RH carbon exhibit sufficient wear resistance. A Raman spectroscopic analysis on the worn surface of a steel ball revealed that the transfer layer at 600 °C included less graphitic structure, compared to the other carbonizing temperature. Based in these findings, we recommended an optimal carbonizing temperature for applications as a sliding material exposed to dry sliding contact.

Keywords: Carbon, Graphite; Unlubricated Friction; Unlubricated Wear; Adhesion; Self Lubrication Friction; Solid/Self Lubrication, Raman, XRD; Adhesive Wear

INTRODUCTION

Rice husk (RH) is the hard outermost shell of rice grains, generally produced as the main by-product of rice milling. It is rich in organic compounds, such as cellulose and lignin, and contains considerable amorphous silica (1–4). Therefore, RH is not edible for humans. Milled RH is commonly used in agriculture and livestock industries and as a soil reformer, mulch for cultivation, bedding material, feed for domestic animals, and compost material (5). On the other hand, it has a promising potential as an engineering material due to its structural characteristics and consistent availability. RH contains carbon and silicon can be considered a carbon–silicon composite. RH has been extensively investigated in terms of its chemical, mechanical, electrical, and tribological properties.

The controlled burning of RH in air yields white RH ash, which contains considerable silica (more than 95% by mass). This technique is considered a cheap alternative to conventional methods of producing various ceramic powders and other silicon-containing materials such as zeolite, cordierite, magnesium silicide, sodium silicate, silanes, forsterite, pure silica, and high-purity silicone (6–16). RH can be carbonized in an inert gas environment to form black ash, which is essentially a uniformly mixed and highly porous carbon-silica powder. Black ash is considered a very useful and economical starting material for synthesizing materials such as silicon tetrachloride, silicon carbide, and silicon nitride (17–22). The principle of obtaining carbon/silica powders by the carbonization of RH in inert gases has been used in several studies to synthesize various composite materials (23–30). On the other hand, the presence of silicon significantly affects (generally improves) the

tribological performances of some Si-containing tribomaterials including silicon nitride and Si-containing diamond-like carbon (31–37). Therefore, the development of a novel tribomaterial derived from RH is a promising area of research.

A novel tribomaterial is RH-based carbon, called RH carbon, which have been developed and investigated extensively (38–41). In a previous study, the tribological behaviors of RH carbon disks against an austenitic stainless-steel ball were investigated under dry conditions and in the presence of water as a lubricant (38). The RH carbons were manufactured by carbonizing a mixture of liquid phenol resin and milled rice husk powder in an argon atmosphere at a certain pre-carbonizing temperature; then, the carbonized powder was mixed again with powdery phenol resin and re-carbonized in an argon atmosphere. The two-stage carbonizing process allowed small shrinkage and prevention of catastrophic cracks of samples and reduction of total carbonizing time, because large shrinkage of volume by pyrolysis was completed in the first carbonizing process. According to the results of the study (38), the RH carbon samples that were carbonized at 900°C exhibited a low friction coefficient (<0.11) and low specific wear rate ($<1.5 \times 10^{-6}$ $mm^3/N \cdot m$) under dry conditions and a slightly higher friction coefficient and wear were rate with water lubrication. Furthermore, Tuvshin et al. (39) investigated the effects of the pre-carbonizing temperature on the friction and wear behaviors of RH carbon disks against an austenitic stainless-steel ball. The results showed that the RH carbons that were carbonized at a pre-carbonizing temperature of 900°C demonstrated superior tribological behavior than those carbonized at 1400°C and 1500°C. Thus, it was concluded that the low friction and low wear rate were due

to the presence of a transfer film on the RH carbon comprising amorphous silica and amorphous carbon. Another study revealed the effects of the use of counterpart materials (40). When the disk sample was the RH carbon that was carbonized at a pre-carbonizing temperature of 900°C, high-carbon-chromium bearing-steel balls and austenitic stainless-steel balls had lower friction coefficients (<0.11) and lower specific wear rates than alumina balls. However, in these studies, the re-carbonizing temperature was fixed at 900°C and the carbon parts of the RH carbon disks were not exposed to high temperatures during the manufacturing process. Therefore, Shibata et al. (41) studied RH carbon carbonized at higher temperatures during the re-carbonizing process rather than during the pre-carbonizing process. The results of this study indicated that RH carbon carbonized at a re-carbonizing temperature of 1400°C exhibited extremely low friction coefficients (<0.10) against stainless-steel balls at low contact pressures even under dry conditions, which exist when the sample is exposed to a room atmosphere.

In the re-carbonizing process, high carbonizing temperatures are considered to lead to high energy consumption and time inefficiency. Therefore, in this study, we aim to clarify the effect of re-carbonizing temperature on the microstructural, mechanical, and tribological properties of RH carbon. Furthermore, we discuss the relation between the microstructural and mechanical properties and the tribological behaviors.

EXPERIMENTAL DETAILS

Material preparation

RH carbon was fabricated using the manufacturing process established in a previous study

(38), as shown in Fig. 1. First, milled rice husk powder was mixed with liquid phenol resin at a mass ratio of 3:1. The mixture was then dried and pre-carbonized in an argon atmosphere at 400°C. At this temperature, the phenolic resin is likely to undergo either cyclization or aromatization, while the cellulose in the rice husk begins to form a polyaromatic structure by dehydration at 150–240°C following breakages of the carbon-carbon chain (42). The pre-carbonized mixture was then crushed and sifted through a screen to obtain particles with an average size of less than 150 μm. Then, the carbonized powder was again mixed with powdery phenol resin in a 3:1 mass ratio. This secondary mixture was pressed into a disk shape (called the precursor). Finally, the molded disk was re-carbonized in a furnace in an argon atmosphere at a temperature (*T*) of 600°C, 800°C, 900°C, 1000°C, 1200°C, 1300°C, or 1400°C under unconstrained conditions. The hold time of the predetermined temperatures was 2 h, irrespective of pre- and re-carbonizing process. The temperature ramp rates were 30 °C/min at below 500 °C and 60 °C/min at above 500 °C.

Analysis of microstructural and mechanical characteristics

The microstructural morphologies of the RH carbon samples were observed by scanning electron microscopy (SEM) coupled with energy-dispersive X-ray spectroscopy. Raman spectroscopic analysis was used to characterize the carbon in the RH carbon. The Raman spectra were obtained using a micro-Raman spectrophotometer system with a laser wave length of 532 nm and a laser power of 100 mW. X-ray diffraction (XRD) analysis was used to characterize the constituent phases in the RH carbon samples. The XRD patterns were obtained using a diffractometer with Cu Kα radiation, a tube current of 40 mA, and a tube

voltage of 40 kV.

The mechanical properties—shrinkage rate, density, elasticity, strength, hardness, and surface roughness—of the RH carbons were measured. The bulk density was measured as the ratio between the measured weight and bulk volume of each sample. Compression tests were conducted using a uniaxial compression-testing apparatus at a crosshead speed of 8.3 μm/s to obtain the elastic modulus and compressive strength of each sample. The hardness values of the RH carbon samples were determined using the micro-Vickers indentation method with a loading force of 0.98 N and loading time of 20 s. The surface roughness of each RH carbon sample was measured using profilometer after polishing with #2000 waterproof abrasive paper.

Tribological testing

Friction tests were conducted using a ball-on-plate-type friction tester under dry conditions in a laboratory. Figure 2 illustrates the friction-testing apparatus. The RH carbon samples were attached to the underlying stage and an 8-mm-diameter martensitic stainless-steel ball (JIS SUS440C) with an elastic modulus of 200 GPa, Vickers hardness of 6.7 GPa, and surface roughness (R_a) of 0.14 μm was fixed to the upper arm using a ball holder. Before each sliding test, the ball and the disk specimens were ultrasonically cleaned in hexane for 5 min, and then dried under a weak vacuum. Then, the ball and sample were brought into contact such that the ball applied a normal load of 1.0, 2.0, 4.9, or 9.8 N to the sample. The stage was moved along a line perpendicular to the axis of the arm under dry conditions to slide the ball across the sample at a velocity of 10 mm/s for 2×10^4 friction cycles. The tests were

conducted at a relative humidity of 40 ± 5% and a laboratory temperature of 20 ± 2°C.

The friction force was measured using a load cell coupled to the upper arm and used to calculate the friction coefficient of each sample. The wear volume and specific wear rate for each specimen were calculated based on the cross-sectional area of the wear track as measured using a profilometer. The specific wear rate was calculated according to the following equation:

$$ws = \frac{V}{L \cdot W} \quad (1)$$

where, ws is the specific wear rate ($mm^3/N \cdot m$), L is the sliding distance (m), and W is the normal load (N).

RESULTS AND DISCUSSION

Microstructural and mechanical characteristics

Figure 3 shows SEM images and elemental maps of the RH carbon samples carbonized at 600°C, 1000°C, and 1300°C. The pore size and the number of pore increased as the carbonizing temperature increased. The fraction of the constituents among all samples was almost the same as 83at% of carbon, 10at% of silicon, and 6at% of oxygen.

Figure 4 shows the Raman spectra of RH carbon samples. Two broad band peaks were observed for each sample, indicating the presence of amorphous carbon structures. To separate the two broad peaks, curve fitting was conducted to fit the data to three Gaussian functions to avoid overfitting. a representative curve-fitting result is shown in Fig. 5. The

wave numbers of the peaks were 1332, 1377, and 1583 cm^{-1}. The peak at 1583 cm^{-1} indicated the presence of a hexagonal carbon lattice, called the G-band (43). However, the peaks at 1332 and 1377 cm^{-1} could not be well explained; the peaks might have arisen from a structural defect in the hexagonal graphite lattice, interfusion of an inorganic compound (such as a phosphate or magnesium compound), or binding of carbon and silica. Table 1 shows the rates of integral intensity for the G-band calculated from the fitted curves. The rates decreased as the carbonizing temperature increased from 600°C to 800°C, increased as the carbonizing temperature further increased from 800°C to 1000°C, and then converged to a stable value at higher carbonizing temperatures. This indicates that the carbonizing process was transitive in the temperature range of 600°C to 1000°C and the structural transition of the carbon component was small at temperatures above 1000°C.

Figure 6 shows the XRD patterns of RH carbon samples carbonized at different temperatures. The XRD pattern of the samples carbonized at 1300°C and 1400°C had sharp peaks at a 2θ angle of approximately 21°, which is characteristic of a polymorphic crystal of silica (cristobalite), superimposed on a broad background induced by the remaining amorphous carbon and silica (21,44). Moreover, the XRD patterns of the samples carbonized at 1300°C and 1400°C had sharp peaks at approximately 36°, implying the formation of small amounts of silicon carbide. In contrast, the XRD patterns of the samples carbonized at temperatures below 1200°C showed no evidence to indicate the formation of a crystalline phase.

Figure 7 shows the mechanical properties of the RH carbon samples carbonized at

different temperatures. The values for shrinkage rate, density, elastic modulus, and compressive strength were the mean values obtained from five tests and the Vickers hardness values were calculated as the mean value from 20 tests; the error bars indicate the standard deviations of these measurements. The shrinkage rate and bulk density increased as the carbonizing temperature was increased from 600°C to 1200°C, indicating that the densification occurred in this temperature range. Volatile silicon monoxide and carbon monoxide are produced in the chemical reaction between the silica and carbon contained in the rice husk material when it is carbonized at 1400°C (28). The presence of these volatile reactants decreased the bulk density of the RH carbon samples. In pyrolysis process of phenol resin, a pyrolysis gas generates massively at within 350–600°C. The precursor included pure phenol resin even after the press forming. Therefore, the density of the sample re-carbonized at 600°C was lower than the precursor. The elastic modulus measurements showed large standard deviations and didn't exhibit statistically any differences between the samples including the precursor. The precursor had a much higher strength than the re-carbonized RH carbons, which were brittle. However, the RH carbons were harder than the precursor. This was attributed to the densification in the carbonizing temperature range of 600–1200°C and the formation of hard crystalline silica at the carbonizing temperatures of 1300°C and 1400°C. The surface roughness exhibited almost the same trend except for the sample carbonized at 1400°C, which had a two-times greater surface roughness than the other samples. This surface roughness was attributed to the presence of volatile reactants and hard crystalline silica despite polishing.

Friction and wear properties

Figure 8 shows the friction coefficients of the RH carbon samples as functions of the number

of friction cycles applied at normal loads of 1.0 and 4.9 N. The friction coefficient of the precursor gradually increased with repeated friction cycles at 1.0 N (Fig. 8(a)) and rapidly increased with the repeated cycles at 4.9 N, reaching a high stable value (Fig. 8(b)). In Fig. 8(a), the RH carbon samples carbonized at temperatures in the range of 800–1200°C had low and stable friction coefficients of 0.10–0.15, while the friction coefficients of the RH carbon samples carbonized at 1300°C and 1400°C were smaller. At a normal load of 4.9 N (Fig. 8(b)), the RH carbon samples carbonized at high temperatures in the range of 1200–1400°C also had low friction coefficients (≤0.10).

Figure 9 shows the relation between the mean friction coefficient and carbonizing temperature. The mean friction coefficient was calculated as an average of those measured over all 2×10^4 friction cycles and the error bars indicate the maximum and minimum measured values. At low normal loads of 1.0 and 2.0 N, the mean friction coefficients decreased as the carbonizing temperature was increased from 600°C to 800°C, remained stable at intermediate carbonizing temperatures in the range of 800–1200°C, and again decreased as the carbonizing temperature increased further from 1200°C to 1400°C. At a normal load of 4.9 N, the mean friction coefficients decreased as the carbonizing temperature increased from 600°C to 1000°C and was very low (around 0.10) in the samples carbonized at higher temperatures. On the other hand, the RH carbon samples tested with a high normal load of 9.8 N also had the low friction coefficients excepting for the samples carbonized at 600°C.

Figure 10 shows the relation between the specific wear rate and carbonizing

temperature. The error bars indicate the standard deviation in eight measurement points. The wear rates of all samples were below 10^{-5} $mm^3/N \cdot m$, indicating that the re-carbonized RH carbon had sufficient wear resistance against friction under dry conditions. The specific wear rates tended to decrease with increasing normal loads but were not drastically affected by the carbonizing temperature.

Characteristics of the worn surface

To discuss the difference in the friction behavior of samples carbonized at different temperatures, especially at high normal loads, the worn surfaces of the RH carbon were visually observed after the test. Figure 11 illustrates the optical images of the worn surfaces of the RH carbon samples carbonized at 600°C, 900°C, and 1400°C after conducting the high-load (9.8 N) friction tests. The pores in the worn surfaces of all samples appeared to be filled with wear debris. Line scars were observed in all the RH carbon samples, while the number of the scars in the samples carbonized at 1400°C seemed to be smaller than the others. A wear scar on the steel ball was also observed, as shown in Fig. 12. The worn area in which the wear scars were formed on the ball sliding over the surface was greater in the sample carbonized at 600°C than in the other samples. In addition, transfer films were observed on all worn surfaces. Based on the adhesive friction theory (45), the friction force (F) can be expressed as a product of shear strength (τ) and contact area (A), except for a plowing term. Therefore, the friction coefficient is equal to the product of these parameters ($\tau \cdot A$) divided by the applied normal load (W). In this study, the plowing term of the friction force was considered negligible because the wear rates were very low and the steady-state friction was fairly constant. For the same reason, the surface roughness of the hard stainless-ball was

lower than that of the RH carbon sample. On the other hand, both the shear strength and contact area were found to be influenced by the carbonizing temperature. The apparent contact areas were calculated from the optical images of the ball as it was assumed that the worn area is approximately equal to the contact area. It is noted that real contact areas are typically much smaller than apparent contact areas which are measured from clearly visible wear scars, debris, and transfer films.

The apparent contact areas are shown in Fig. 13. The error bars indicate the estimated error as propagated uncertainty from contact width. These apparent contact areas were larger (more than twice) than estimated Hertzian contact area due to wear. With normal loads of 1.0 and 2.0 N, the contact areas were almost the same (approximately 0.05 mm^2) regardless of the carbonizing temperature. However, the contact area increased with higher normal loads. With a normal load of 4.9 N, the contact areas for the RH carbon samples carbonized at 600°C and 1400°C were slightly greater than those for the samples carbonized at other temperatures. With a normal load of 9.8 N, the contact area gradually decreased as the carbonizing temperature was increased from 600°C and 1200°C but increased as the carbonizing temperature was further increased from 1200°C to 1400°C. Figure 14 shows the relation between the apparent shear strength and carbonizing temperature. The apparent shear strength was calculated as the friction force at 2×10^4 cycles divided by the apparent contact area. The error bars indicate the estimated error as propagated uncertainty. The apparent shear strength varied with carbonizing temperature depending on the normal load: particularly at 9.8 N, the apparent shear strength changed drastically with the carbonizing temperature. At a normal load of 1.0 N, the apparent shear strength peaked in the samples

carbonized at 1000°C–1200°C. At normal loads of 2.0 and 4.9 N, the observed changes in shear strength as a function of carbonizing temperature was almost the same: gradually decreasing with increasing carbonizing temperature. With a normal load of 9.8 N, the shear strength was extremely high in the sample carbonized at 600°C, while that in the sample carbonized at 1400°C was less than half this value.

To characterize the difference in the shear strengths of the RH carbon samples worn at high normal loads, Raman spectroscopic analyses were conducted at the centers of the worn surfaces of the steel balls depicted in Fig. 12, as shown in Fig. 15. Two broad peaks similar to those shown in Fig. 4 were observed in all samples at different carbonizing temperatures. This indicates that a transfer film from the RH carbon formed on the steel balls. The rates of the integral intensities of the G-bands of the transfer layers were calculated by curve fitting with a Gaussian function; the results are shown in Table 2. Compared to the disk samples tested before the friction testing (Table 1), the transfer layers had lower rates of integral intensities. In addition, the rate for the transfer layer from the sample carbonized at 600°C was smaller than the others, indicating that this transfer layer had less-graphitic structure. Therefore, it was concluded that the RH carbon sample carbonized at 600°C retained a relatively high shear strength after sufficient friction was applied. The high shear strength despite large contact area was likely to be leading to a high friction coefficient. On the other hand, the rate of the integral intensity of the G-band for the transfer layer from the samples carbonized at 1400°C was almost the same as that from the sample carbonized at 900°C. However, the apparent shear strength of the sample carbonized at 1400°C was smaller than that of the sample carbonized at 900°C. This can be explained by the lower real contact area

on the sample carbonized at 1400°C compared to that of the sample carbonized at 900°C. The sample carbonized at 1400 °C had a lower density, greater porosity, and higher hardness than that carbonized at 900°C. These high porosity and high hardness could lead to the small real contact area even though the apparent contact area was large. Therefore, the real shear strength and real contact area were considered approximately the same for both RH carbons carbonized at 900°C and 1400°C.

Considering applications to use as a sliding material, it is recommended that RH carbon be carbonized at temperatures above 800°C because the friction coefficient was found to be less than 0.15 and the specific wear rate was found to be less than 3×10^{-6} $mm^3/N\cdot m$. From the viewpoint of the energy consumption in the manufacturing process, carbonization of RH carbon at 800°C is again strongly recommended. However, if high hardness is required, carbonizing temperatures in the range of 1300–1400°C can be used.

CONCLUSIONS

In this study, RH carbon was fabricated at several carbonizing temperatures, and the microstructural, mechanical, and the tribological behaviors of the obtained samples were investigated. Based on the results, the following conclusions can be drawn:

1. The RH carbon exhibited amorphous carbon structures regardless of the carbonizing temperature. The rate of the integral intensity of the G-band, as calculated from the Raman spectra, decreased as the carbonizing temperatures was increased from 600°C to 800°C and increased as the carbonizing temperature was further increased from 800°C

to 1000°C, and then converged at a certain value with higher carbonizing temperatures.

2. The XRD patterns of RH carbon samples carbonized at 1300°C and 1400°C exhibited sharp peaks at 2θ angles of approximately 21°, implying the formation of a polymorphic crystal of silica.
3. The bulk density similarly increased as the carbonizing temperatures was increased from 600°C to 1200°C due to densification. The hardness also increased with carbonizing temperatures due to densification in the carbonizing temperature range of 600–1200°C and due to the formation of the hard crystalline silica in the carbonizing temperature range of 1300–1400°C.
4. At low normal loads of 1.0 N, 2.0 N, and 4.9 N, the mean friction coefficients tended to decrease as the carbonizing temperature increased from 600°C to 800°C and gradually decrease as the carbonizing temperature increased from 800°C to 1400°C. At a high normal load of 9.8 N, the RH carbon samples exhibited low friction coefficients (around 0.10) except for the sample carbonized at 600°C.
5. The wear rates of all samples were below 10^{-5} $mm^3/N \cdot m$, indicating that the RH carbon exhibited sufficient wear resistance against friction under dry conditions.
6. The shear strength of the RH carbon samples gradually decreased as the carbonizing temperature increased with a high normal load of 9.8 N. The shear strength of the sample carbonized at 600°C was extremely high, while that of the sample carbonized at 1400°C was less than this value. The Raman spectroscopic analysis of the worn surface of the steel ball revealed that the transfer layer from the samples carbonized at 600°C had a less-graphitic structure. Therefore, the RH carbon samples carbonized at 600°C retained a relatively high shear strength after sufficient friction was applied.

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Table Captions

Table 1 Rates of integral intensity of the G-bands from curves fitted to the Raman spectra of samples carbonized at different temperatures.

Table 2 Rates of the integral intensities of the G-bands for the transfer layers.

Figure Captions

Fig. 1. Manufacturing process for RH carbon.

Fig. 2 Friction testing apparatus.

Fig. 3 Representative SEM images and the elemental maps of RH carbon carbonized at (a) 600°C, (b) 1000°C, and (c) 1300°C.

Fig. 4 Raman spectra of RH carbon samples carbonized at different temperature.

Fig. 5 Representative curve fitting to the Raman spectrum of an RH carbon sample carbonized at 1400°C.

Fig. 6 XRD patterns of RH carbon samples carbonized at different temperatures.

Fig. 7 Mechanical properties of RH carbon: (a) volume shrinkage rate, (b) density, (c) elastic modulus, (d) compressive strength, (e) Vickers hardness, and (f) surface roughness.

Fig. 8 Typical changes in the friction coefficient of RH carbon sample over repeated friction cycles at normal loads of (a) 1.0 N and (b) 4.9 N.

Fig. 9 Relation between the mean friction coefficient and carbonizing temperature.

Fig. 10 Relation between the specific wear rate and carbonizing temperature.

Fig. 11 Optical images of the worn surfaces of RH carbon samples carbonized at (a) 600°C, (b) 900°C, and (c) 1400°C following the high-load tests (normal load of 9.8 N).

Fig. 12 Optical images of the wear scars on the steel balls after the high-load tests (normal load of 9.8 N) corresponding to the RH carbon carbonized at (a) 600°C, (b) 900°C, and (c) 1400°C.

Fig. 13 Apparent contact areas calculated from the area of the wear scar.

Fig. 14 Relation between the apparent shear strength and carbonizing temperature.

Fig. 15 Raman spectra collected from the centers of the wear scars of the balls shown in Fig. 12 from the samples carbonized at (a) 600°C, (b) 900°C, and (c) 1400°C.